

## Formation of electrodeposited Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating: effect of Si<sub>3</sub>N<sub>4</sub> concentration

E Budi<sup>1,2\*</sup>, I Sugihartono<sup>1</sup>, W Indrasari<sup>1</sup>, Y Ermadiana<sup>1</sup>, D Syafindra<sup>1</sup>, A Fikry<sup>1</sup>, and Y Oktaviani<sup>1</sup>

<sup>1</sup> Physics Program, Faculty of Mathematics and Science, Universitas Negeri Jakarta, Jl. Rawamangun Muka I, Jakarta 13220, Indonesia

<sup>2</sup> Physics Education Program, Faculty of Mathematics and Science, Universitas Negeri Jakarta, Jl. Rawamangun Muka I, Jakarta 13220, Indonesia

\*esmarbudi@unj.ac.id

**Abstract.** The Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating has been investigated. The composites were deposited at fixed electrodeposition current of 3 mA for 15 minutes. The electrolyte consists of 0.49 mol/l H<sub>3</sub>BO<sub>3</sub>, 0.17 M NiCl<sub>2</sub>·6H<sub>2</sub>O, 0.38 M NiSO<sub>4</sub>·6H<sub>2</sub>O, 0.2 gr/lit SDS, 2 gr/lit AlN and 2 gr/lit TiN. The concentration of Si<sub>3</sub>N<sub>4</sub>nanofiber was varied into 10, 20 and 30 gr/lit. The electrodes used were Pt wire as counter electrode, AgClwire as reference electrode and tungsten carbide (WC) rod as working electrode. The surface morphology and composition of composites were characterized by using Scanning Electron Microscopy (SEM) dan Energy Dispersive Spectroscopy (EDS), respectively. The crystal structure of composites was characterized by using X-Ray Diffraction (XRD) and the hardness was tested by using Vickers hardness tester. The results showed that the composite coating surface morphology was finer as the increase of Si<sub>3</sub>N<sub>4</sub> concentration due to the decrease of Ni crystal size. The increase of S<sub>3</sub>N<sub>4</sub> concentration indicating the formation of stable structure composed of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> caused the increase of the coating hardness.

### 1. Introduction

Ni-nitride electrodeposition is an attractive method in improving the properties of composite coating such as mechanical and corrosion resistance [1]. The improvement is achieved by homogenous dispersion of nitride particles into the nickel matrix [2,3]. In early studies, the formation of super hard nanocomposite nitride/Si<sub>3</sub>N<sub>4</sub>by using Chemical Vapor Deposition has been performed and it was reported that maximum hardness is achieved when the nitride crystals are covered with Si<sub>3</sub>N<sub>4</sub> monolayer [4]. Silicon nitride is one of the strongest ceramic material and has being used as reinforced material in the composite coating by using electrodeposition method [5]. The incorporation of silicon nitride in the electrodeposited composite coating showed improving coating properties especially in microhardness and corrosion resistance.

Recently, the electrodeposition method has been utilized to deposit Ni-TiAlN composite [6]. Electrode potion of Nickel (Ni) is one of the common process due to so many its industrial applications since it has good corrosion resistance and microhardness [7]. Incorporation of nitride particle into Ni coating has improved its hardness and corrosion resistance. It is known that nitride particle such as TiAlN is one of the hard particles with high thermal stability [8].



The investigation on Si<sub>3</sub>N<sub>4</sub> compound showed a good hardness and wear resistance in composite coating [9]. Another investigation reported that the decrease of particle size of silicon nitride within the Ni metal matrix will lead to higher corrosion resistant [10]. Si<sub>3</sub>N<sub>4</sub> particles are filling pores and mainly inert incorporated into the coating surface due to high melting point and eventually improve its corrosion resistance [11].

Previously review study has been done in searching a new possibility electrodeposited composite coating system [12]. In this research, a new Ni-nitride composite coating system of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> has been experimentally investigated. The objective of this experiment is to investigate the effect of Si<sub>3</sub>N<sub>4</sub> concentration on morphology, composition and crystal structure of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating. Discussion on composite coating hardness also is presented.

## 2. Experiment

In the present work, the Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coatings were electrodeposited at fixed current of 3 mA, 12 V for 15 minutes. The electrolyte consists of 0.49 mol/l H<sub>3</sub>BO<sub>3</sub>, 0.17 M NiCl<sub>2</sub>·6H<sub>2</sub>O, 0.38 M NiSO<sub>4</sub>·6H<sub>2</sub>O, 2 gr/lit AlN, 2 gr/lit TiN and 0.2 gr/lit Sodium Dodecyl Sulfate (SDS). Si<sub>3</sub>N<sub>4</sub> nanofiber was crushed by mortar and was added into electrolyte. The concentration of Si<sub>3</sub>N<sub>4</sub> was varied at 10, 20 and 30 gr/lit. Tungsten carbide (WC) bar with 45 mm x 45 mm cross section area were used as working electrode. Pt wire and AgCl wire were used as counter electrode and reference electrode, respectively. The surface morphology and composition of composite coatings were characterized by using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) of Jeol, JED-2300, respectively. The crystal structure of composite coatings were characterized by using X-Ray Diffraction (XRD) of Panalytical Empyrean Philips with Cu-K $\alpha$  radiation source ( $\lambda$  = 1.54 Å) and the composite coatings hardness were measured by using micro hardness Vickers tester HV-1000.

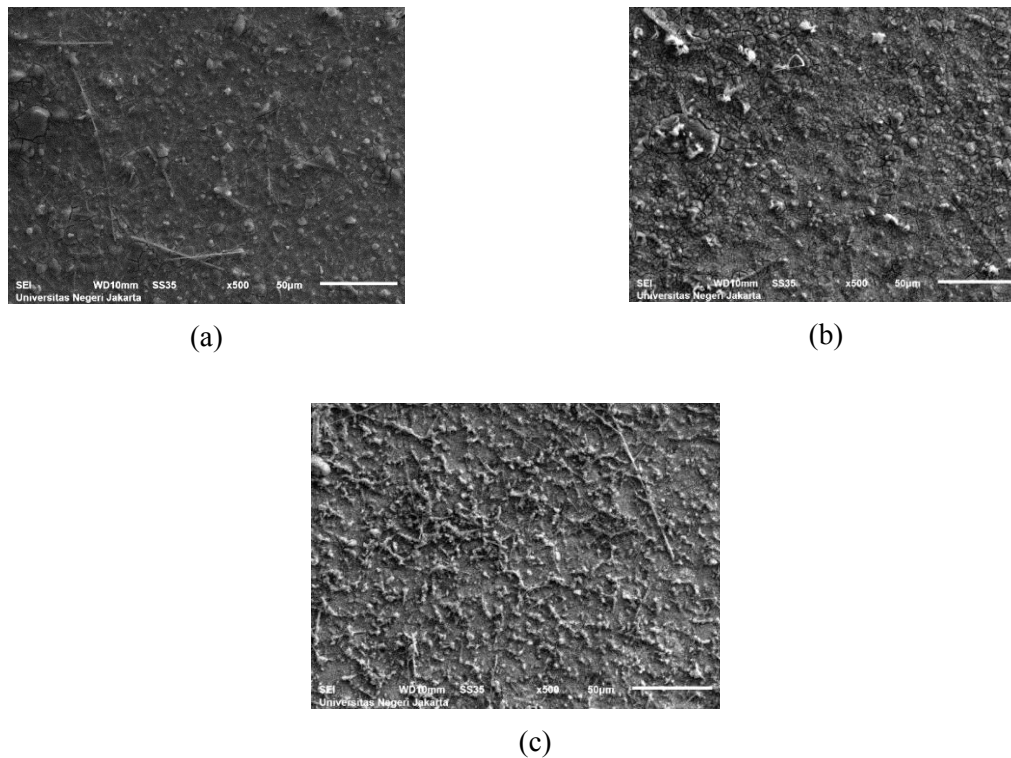
## 3. Results and discussion

### 3.1. Surface morphology and composition

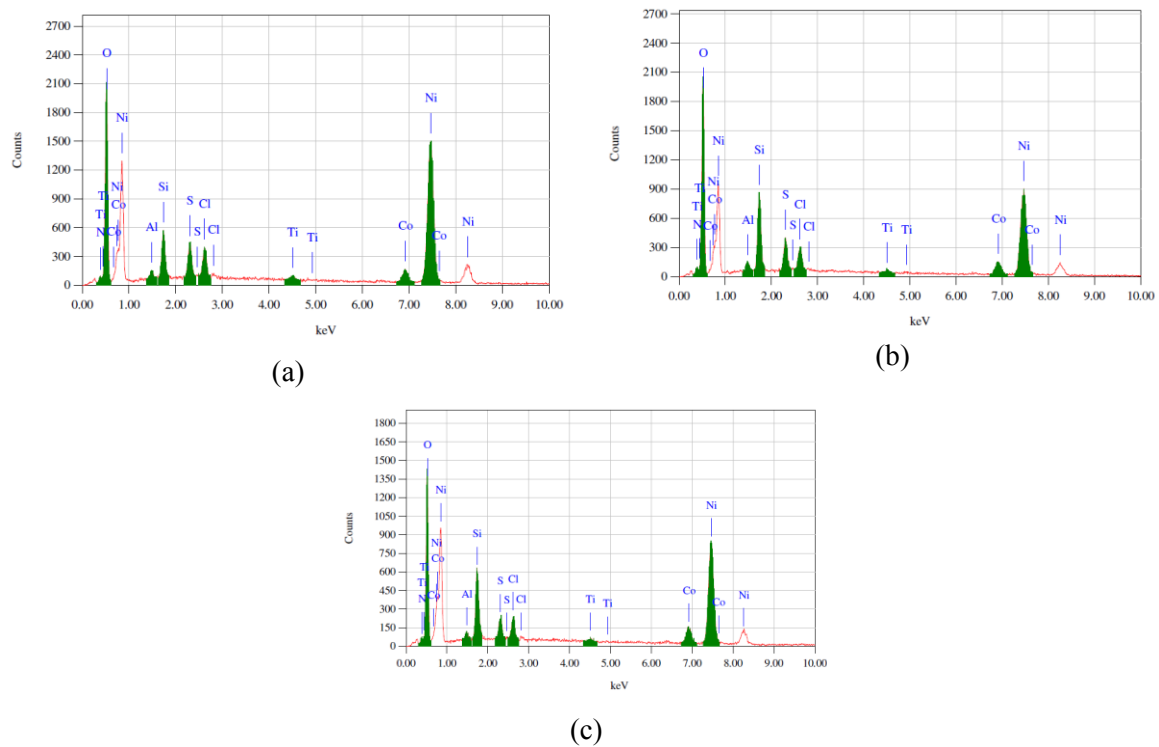
SEM image of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coatings are shown in figure 1. Typically, fine and smooth surface morphology of composite obtained at Si<sub>3</sub>N<sub>4</sub> concentration of 10 gr/lit. TiN and AlN particles appear as slight aggregation granular grains in Ni matrix while Si<sub>3</sub>N<sub>4</sub> fibre exhibit as needle grains. The composite surface become rough as the Si<sub>3</sub>N<sub>4</sub> concentration is increased up to 30 gr/lit. This means that too much Si<sub>3</sub>N<sub>4</sub> concentration may accelerate the agglomeration and gravitational sediment effects [13]. At low concentration, Si<sub>3</sub>N<sub>4</sub> nanofiber effectively inhibited the Ni grain growth. However, it did not happen at higher concentration. Meanwhile, the nitride particle or fiber (e.g. Si<sub>3</sub>N<sub>4</sub>) is inert compound and do not react with other component of the coating [11]. TiN, AlN, TiAlN and Si<sub>3</sub>N<sub>4</sub> as inert compound, may hinder the Ni crystal growth. However, in the formation of TiAlN/Si<sub>3</sub>N<sub>4</sub> coating, the crystal size of coating decrease due to the substitution of Ti by Al or Si [14].

The composition of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coatings are shown in figure 2. From the EDS analysis result, it shows that the content of Ti decreases as the Si<sub>3</sub>N<sub>4</sub> concentration is increased. Although, the binding energies of TiN and AlN is similar however, TiN's binding energy is less than AlN's [14]. Therefore, the number of Ti substitution by Si is higher than Al. As the Si<sub>3</sub>N<sub>4</sub> concentration is increased, thus it increases the substitution of Ti by Si. This causes the decrease of nitride crystal size and increase the Ni crystal growth and finally lead the increase of surface coating roughness.

From EDS result, it shows that the increasing Si<sub>3</sub>N<sub>4</sub> concentration from 20 gr/lit to 30 gr/lit decreases the Si incorporated fraction into the coating. This behaviour might be the effect of collision between particles [5] with increasing Si<sub>3</sub>N<sub>4</sub> concentration up to 30 gr/lit.



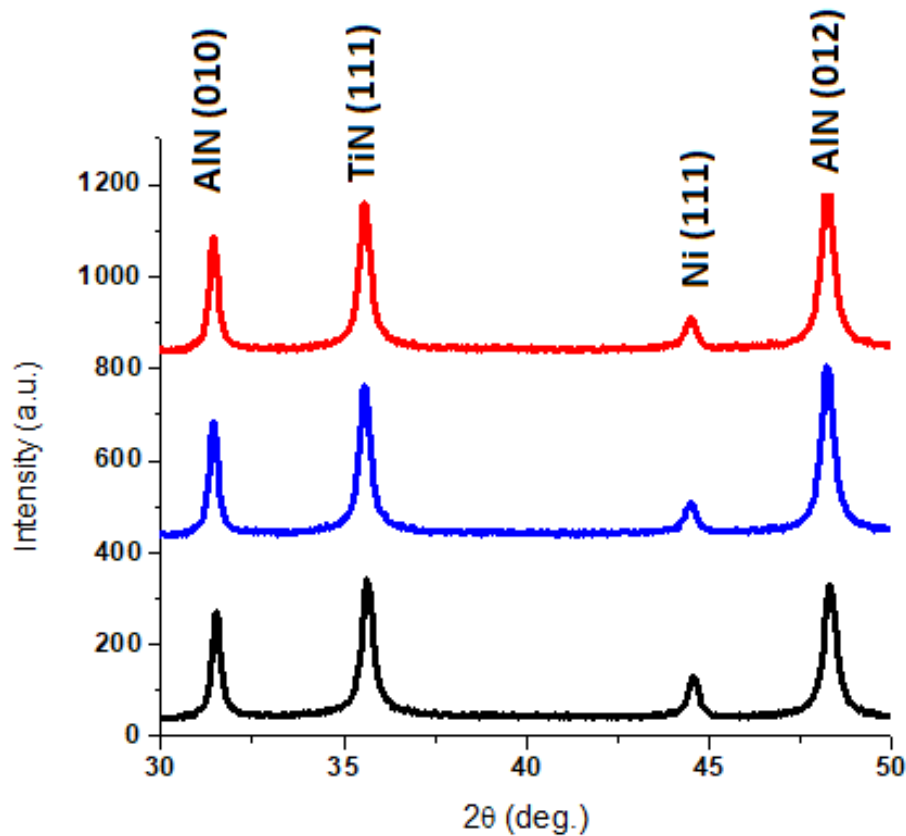
**Figure 1.** Surface morphology Ni-TiAlN/ Si<sub>3</sub>N<sub>4</sub> composite coating deposited at Si<sub>3</sub>N<sub>4</sub> concentration of (a) 10 gr/lit, (b) 20 gr/lit, (c) 30 gr/lit.



**Figure. 2.** EDS analysis of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coatings at Si<sub>3</sub>N<sub>4</sub> concentration of (a) 10 gr/lit, (b) 20 gr/lit, (c) 30 gr/lit.

### 3.2. Crystal structure

XRD spectrum pattern of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating in varying Si<sub>3</sub>N<sub>4</sub> concentration is shown in figure 3. The high peaks intensity at  $2\theta = 31.50$  and  $2\theta = 48.30$  are assigned to AlN (010) and AlN (012), respectively while the peak at  $2\theta = 35.60$  is assigned to TiN (111). The lower peak at  $2\theta = 44.60$  is assigned to Ni (111). Si<sub>3</sub>N<sub>4</sub> peak is not revealed in the composite due to its amorphous nature [14,15]. The peak intensity of Ni (111) decreases drastically as the Si<sub>3</sub>N<sub>4</sub> concentration is increased up to 20 gr/lit and it slightly increases as further increasing in Si<sub>3</sub>N<sub>4</sub> concentration. The decrease of Ni (111) peak is followed by the peak broadened indicating the decrease of its crystal size. On the other hand, the crystal size of TiN and AlN increases gradually as the Si<sub>3</sub>N<sub>4</sub> concentration is increased up to 20 gr/lit and it decreases as further increasing in Si<sub>3</sub>N<sub>4</sub> concentration. The decrease of Ni crystal size may presumably due to the incorporation of amorphous Si<sub>3</sub>N<sub>4</sub> and the crystal growth of TiN and AlN in Ni matrix. The XRD data shows that the Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating consists of Ni, TiN and AlN crystal and amorphous phase of Si<sub>3</sub>N<sub>4</sub>. This behaviour was also reported for another composite coating [14,15].



**Figure 3.** XRD analysis of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coatings at Si<sub>3</sub>N<sub>4</sub> concentration of (a) 10 gr/lit, (b) 20 gr/lit, (c) 30 gr/lit.

### 3.3. Hardness

The hardness test results of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> are shown in Table 1. An increase of hardness with increasing Si<sub>3</sub>N<sub>4</sub> concentration from 10 gr/lit to 20 gr/lit occurs. This might be attributed by Ni grain refining and crystal growth of TiN and AlN due to the increase of Si<sub>3</sub>N<sub>4</sub> incorporation into the coating. It is caused by the hindering dislocation motion by amorphous Si<sub>3</sub>N<sub>4</sub> phase. The decrease in Ni crystal size indicates the formation of stable structure composed of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub>. The increase of composite coating hardness was also reported by other types composite coating [16,17].

**Table 1.** Experimental result of Vickers hardness test of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating at various Si<sub>3</sub>N<sub>4</sub> concentration.

No	Si <sub>3</sub> N <sub>4</sub> Concentration (gr/lit)	HVN (kg/mm <sup>2</sup> )
1	10	914
2	20	1187
3	30	1025

However, the hardness slightly decreases as further increasing Si<sub>3</sub>N<sub>4</sub> concentration up to 30 gr/lit as decreasing Si incorporation fraction into the coating. It was reported that the composite coating hardness decreased significantly with further increase Si content due to the increase in the amorphous Si<sub>3</sub>N<sub>4</sub> in TiAlN matrix [14,15]. The further increase in amorphous Si<sub>3</sub>N<sub>4</sub> caused the very small crystal size of composite then it was not effectively in hindering the dislocation motion.

#### 4. Conclusions

The formation of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub> composite coating is possibly produced by using electrodeposition process. The improve of coating hardness at the increase of Si<sub>3</sub>N<sub>4</sub> concentration is due to the decrease of coating crystal size especially Ni crystal indicating the formation of stable structure composed of Ni-TiAlN/Si<sub>3</sub>N<sub>4</sub>.

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#### References

- [1] F F Xia, W Yue, J Wang, C Liu, F Wang, Y Lia and Ceram 2015 **41** 11445–11448
- [2] M Wu, W Jia and P Lv 2017 *Proc. Eng.* **174** 717 – 723
- [3] F Xia, H Xu, C Liu, J Wang, J Ding, and C Ma 2013 *Appl. Surf. Sci.* **271** 7– 11
- [4] S Veprek, G J Maritz and V -Heijman 2007 *Surf. Coat. Technol.* **201** 6064–6070
- [5] A Robin, J C P Santana and A F Sartori 2011 *Surf. Coat. Technol.* **205** 4596–4601
- [6] E Budi, Y Ermadiana, I Sugihartono, D Syafindra and M Fajrin 2017 *Int. Sym. Mater. Electrical Eng. Bandung*
- [7] I V Antihovich, N M Ablazhey, A A Chernik and I M Zharsky 2014 *Proc. Chem.* **10** 373 – 377
- [8] L Chen, J Paulitsch, Y Du and P H Mayrhofer 2012 *Surf. Coat. Technol.* **206** 2954–2960
- [9] A C Lee, H H Lu, H T Lin, P Sajgalik, D F Lii, P K Nayak and C Y Chen, J L Huang and J Asian 2015 *Ceram. Soc.* **3** 6–12
- [10] M A Khazrayie and A R S Aghdam 2010 *Trans. Nonferrous Met. Soc. China* **20** 1017-1023
- [11] X Lu, C Blawert, N Scharnagl, K U Kainer and J Magnes 2013 *Alloys* **1** 267-274
- [12] E Budi 2016 *Spektra: J. Fisika Aplikasi* **1**(2) 187-193
- [13] ZHU Xu-bei, CAI Chao, ZHENG Guo-qu, ZHANG Zhao and LI Jin-feng 2011 *Trans. Nonferrous Met. Soc. China* **21** 2216–2224
- [14] H C Barshilia, B Deepthi and K S Rajam 2006 *Vacuum* **81** 479-488
- [15] H C Barshilia, B Deepthi, A S Arun Prabhu and K S Rajam 2006 *Surf. Coat. Technol.* **201** 329–337
- [16] F F, Xia, W Yue, J Wang, C Liu, F Wang and Y Lia 2015 *Ceram. Int.* **41** 11445–11448
- [17] M R Vaezi, S K Sadrnezhad and L Nikza 2008 *Colloids Surf. A: Physicochem. Eng. Aspects* **315** 176–182